Occurrence, composition and dew point of tars produced during gasification of fuel cane bagasse in a downdraft gasifier

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ABSTRACT

Gasification of pelletised fuel cane bagasse a waste residue from an energy crop known as fuel cane was investigated to evaluate the potential of fuelling solid oxide fuel cells (SOFCs) with the raw fuel gas produced. Tars produced during gasification of the bagasse in a 50 kWe air-blown downdraft autothermal gasifier were collected, quantified and characterised and the tar dew point evaluated. The concentration of tar collected was $376 \pm 27 \ \mathrm{mg \, m^{-3}}$ of dry syngas (at 273 K, 101 kPa), emphasising the efficiency of the tar cracking reactions in the oxidation zone of the gasifier. However, although tar production was low, the typical mixture of tar compounds produced exhibited a high tar dew point of $90 \pm 5 \ ^\circ$C and was dominated by Class 2 and 5 tars which condense readily even at low concentrations. Additionally Class 1 tars had a mass fraction of 8% of the total tar produced. Therefore the calculated tar dew point underestimates the actual tar dew point and a high potential for fouling of SOFC anodes exists. Consequently primary or secondary gas cleaning treatment measures targeting the production or occurrence of Class 1, 2 and 5 tars will be essential for long term operation of SOFC power generating systems fuelled by raw fuel gas from fuel cane bagasse.

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1.   Introduction

The major contaminant contained in gasifier raw fuel gas is tar, a complex mixture of more than 10,000 organic compounds which is produced during gasification when solid carbonaceous fuels undergo pyrolysis [1]. Condensation of tars on downstream processes creates operational difficulties leading to clogged fuel lines, cracking in the pores of filters and damaged power conversion systems resulting in unacceptably high levels of maintenance for engines, turbines and fuel cells. Most raw fuel gas applications therefore require the removal of some or all of the tars before the gas can be used [2]. Moreover, they contain on a weight basis, approximately 10% of the total biomass high heating value (HHV) [3] which is lost

to the raw fuel gas if they are not converted to H_2, CO and CH_4. The reduction and/or removal of tar from the raw fuel gas is therefore one of the major technical barriers to be overcome in the development of biomass gasification for the use of this gas in efficient and economic generation of power [4].

The occurrence, composition and concentration of tar formed during gasification are functions of the fuel used and the process variables employed. A large body of information on total tar mass production can be found in the literature, however little information has been reported on tar composition from downdraft gasifiers. Moreover since the quantity and type of tar produced can cause forced-outages in industrial operations due to blocking and fouling of downstream equipment, understanding tar formation and composition

during gasification of biomass is fundamental to the efficient operation of commercial biomass gasification systems.

The term "fuel cane", collectively describes three types of high fibre cane (mass fraction 26–28.3%) developed in Barbados for energy production by the West Indies Central Sugar Cane Breeding Station (WICSCB). These canes designated W179460, W179461 and W181456 were produced by genetic hybridisation of wild *Saccharum spontaneum* clones with very high levels of fibre, and noble and commercial clones of sugar cane [5]. Fuel cane has a low sucrose content (11–11.3%) [6] and is subjected to the same type of processing in sugar factories as sugar cane. Fuel cane bagasse (FCB), the residue from fuel cane processing has been identified as a potential feedstock for fuelling an air-blown downdraft gasifier coupled to a solid oxide fuel cell (SOFC). SOFCs offer the best opportunity to upgrade the low heating value of the raw fuel gas produced by gasification since coupling a gasifier with a fuel cell can potentially achieve fuel conversion efficiencies as high as 60% [7]. This paper discusses the composition and dew point of the tars produced during gasification of FCB in a pilot scale 50 kWe downdraft gasifier and evaluates the feasibility for operation of SOFCs on this biofuel.

2. Experimental

2.1. Preparation of fuel cane bagasse

Fuel cane, grown at various locations in Barbados (13° 10N, 59° 32W) and at elevations ranging from 60 to 90 m was harvested by mechanical harvesters in February during the dry season. They were cut approximately 15 cm above ground and the stalk, cane tops and trash were immediately loaded unto trailers and delivered to the Portvale sugar factory where sugar was extracted within 48 h of harvesting. To avoid changes in biomass structure caused by complete drying, the bagasse produced was then air dried outdoors in covered areas at ambient conditions (32 °C) to a moisture content of mass fraction 20–25%. After drying, the bagasse was sealed in 50 polypropylene bags each weighing 20 kg and shipped to the United Kingdom for use in this study. On arrival at the laboratory in the UK, the FCB was air dried indoors at laboratory-ambient conditions. During this time the heaps were mixed every two days to ensure even drying and the moisture content monitored periodically until equilibrium with the ambient atmosphere (mass fraction 9.4–10%, dry basis) was obtained. It was then shredded in a hammer mill and pelletised into 8 mm diameter pellets using a Swedish Power Chippers AB commercial pellet press PP300, the final moisture content of the pellets ranged from mass fraction 6.0 to 7.4% (dry basis).

2.2. Characterisation of fuel cane bagasse

Sampling of FCB was carried out according to Ref. [8]. Each bag of bagasse was emptied into a heap, the heap was visually divided into three layers and a shovel was used to sample each layer. These samples were mixed to form a composite sample after which subsamples of 100 g each were removed. The subsamples were mixed and samples from this mixture were then used for determination of the mesh size, bulk density, proximate and ultimate analysis using CEN/TS methods [9–12]. Mesh size of the bagasse was determined by hand sieving using Endecott laboratory test sieves. Starting with the largest aperture which retained bagasse, the particles were collected quantitatively through successively smaller sieves until the smallest particles could be retained. Each portion retained in the sieve was weighed to establish the particle size composition. The results of these analyses are presented in Table 1.

2.3. 50 kW(e) air-blown downdraft gasifier

A schematic of the downdraft gasifier system used in this work is shown in Fig. 1. Gasification of the bagasse was carried out at atmospheric pressure in an intensified autothermal air-blown 50 kW(e) throated downdraft gasifier. The system mainly comprises an Imbert type reactor with a throat near the base, an air blower, a gas clean up system consisting of two cyclones, a water scrubber and an ash collector. The basic gasification system was described in Refs. [13,14]. The reactor has a double wall and heat loss is further reduced by fibreglass lagging which covers the outer shell.

Fuel cane bagasse was batch fed manually into the reactor through the hopper at the top; after loading the gasifier the induced draft fan was switched on and the reactor started by manually lighting the air inlet ports with a butane torch. Air, the gasifying agent was then sucked into the gasifier through the main air inlet valve at a controlled flow rate and into the chamber surrounding the throat by the induced draft fan. From there the air then flowed into the oxidation zone through a plane of air nozzles. The raw fuel gas generated in the gasifier was then extracted from the reactor by the suction effect of the induced draft fan. As the solid fuel was converted to raw fuel gas, the fuel bed moved down through the reactor under gravity. The ash and residues of char produced during gasification were emptied into the ash box manually by periodically turning the ash box handle during gasification.

Table 1 – Proximate and ultimate analysis of fuel cane bagasse.

Ultimate analysis	
Carbon, w_C (%)	49.4 ± 0.03
Hydrogen, w_H (%)	6.3 ± 0.3
Oxygen,[a] w_O (%)	53.9 ± 0.5
Nitrogen, w_N (%)	0.30 ± 0.06
Sulphur, w_S (%)	0.07 ± 0.01
Chlorine, w_{Cl} (%)	0.05 ± 0.01
High heating value, HHV (MJ kg^{-1})	18.9 ± 0.3
Low heating value, LHV (MJ kg^{-1})	17.6 ± 0.2
Proximate analysis	
Moisture, $w_{moisture}$ (%)	9.4 ± 0.8
Volatile matter, $w_{volatile\ matter}$ (% db)	65 ± 5
Fixed carbon, $w_{fixed\ carbon}$ (% db)	31 ± 4
Ash, w_{ash} (% db)	3.6 ± 0.7

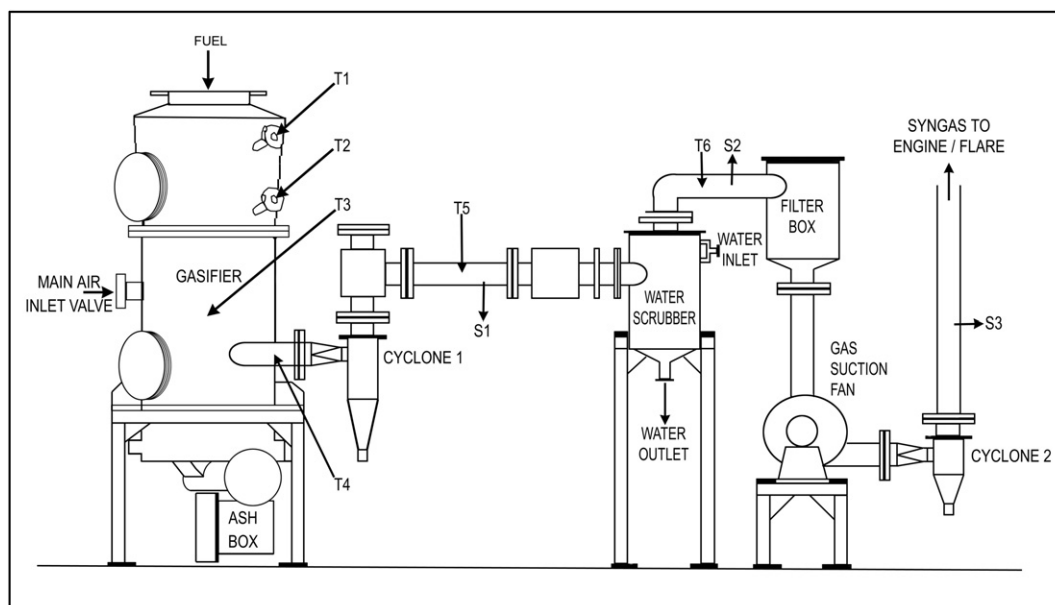db – dry basis.
a Calculated by difference.

Fig. 1 – Newcastle University 50 kWe gasification reactor.

2.4. Experimental conditions

Optimal conditions for gasification of FCB were determined from earlier experiments to be oxidation zone operating temperatures $1040 \pm 130\,°C$, equivalence ratio 0.26 and biomass moisture content of mass fraction 11.5%. On obtaining steady state conditions which were indicated by stability of the raw fuel gas low heating value and the raw fuel gas flow rate, tar sampling was carried out.

2.5. Experimental procedure

2.5.1. Tar collection and storage
Tar sampling was carried out according to the draft Tar Protocol [15] with some modification. Samples of raw fuel gas were extracted at gas tight sample ports under isothermal conditions and at a constant flow rate for a minimum period of 1 h from the raw fuel gas stream at sampling points S2 and S3. To prevent condensation and/or thermal decomposition of target analytes in the sample line, the line was trace heated to $300\,°C$ for the duration of sample collection. The raw fuel gas was then bubbled through a heated glass fibre thimble filter at a flow rate of $0.6\,m^3\,h^{-1}$ (273 K; 101 kPa) into a series of three impinger bottles heated to $40\,°C$ and another three contained in a salt and ice bath at $-12\,°C$. All the impinger bottles contained isopropanol (99.9%), the sampling train used is illustrated in Fig. 2.

On completion of sample collection, the isopropanol in the impingers was mixed, the impingers and tubing were rinsed with additional isopropanol and the rinsate added to the impinger solutions and stored in an air tight brown bottle at $4\,°C$ until the sample could be analysed.

The tar contained in the glass fibre thimble filters was extracted by Soxhlet extraction over a period of five hours using isopropanol. On completion of the extraction, 100 ml of the extract was removed and the remainder added to the stored solution collected from the impingers. After Soxhlet extraction the glass fibre filter thimble was dried in an oven at $105\,°C$ overnight and then cooled in a dessicator. The difference in mass between the initial filter and the extracted filter represents the mass of particulate matter contained in the sampled raw fuel gas. To determine the mass of gravimetric tar contained in the filters, the 100 ml extract was evaporated at $55\,°C$ and 18 kPa using a rotary evaporator. To determine the GC-detectable tar content of the gravimetric tar, the sample was re-dissolved in 25 ml of isopropanol and stored in a sealed brown bottle at $4\,°C$ for analysis.

2.5.2. Gas chromatography/mass spectroscopy (GC/MS)
The sample extracts collected were analysed for tars by gas chromatography/mass spectroscopy (GC/MS) using an HP 5971A GC/MS. The column used was an HP 5MS 30 m × 0.25 mm i.d, 0.25 μm film thickness. The carrier gas was high purity helium (99.999%) at a flow rate of $1.0\,ml\,min^{-1}$. The temperature programme was: initial $50\,°C$ where it was held for 5 min, then to $325\,°C$ at a rate of $8\,°C\,min^{-1}$ where it was held for 5 min. The injector temperature was set at $250\,°C$ and 2 μl of each sample was injected in the split mode with a split ratio of 50:1. The MS was operated in the electron ionization (EI) mode at the electron energy of 70 eV. The transfer line and ion source temperatures were $280\,°C$ and $160\,°C$ respectively. Identification of the tars was done using the NIST spectral library and the MassBank high resolution mass spectral database; quantitative analysis was carried out in full scan mode in the range 50–500 u using internal and external standards.

2.5.3. Fourier transform infrared (FTIR) spectroscopy
FTIR spectroscopy has traditionally been used in wood chemistry to characterise cellulose and lignin qualitatively and quantitatively [16]. Here, a Varian 3100 FTIR was used to investigate the lignocellulosic origin of the tar produced during gasification. Condensed tar samples collected from
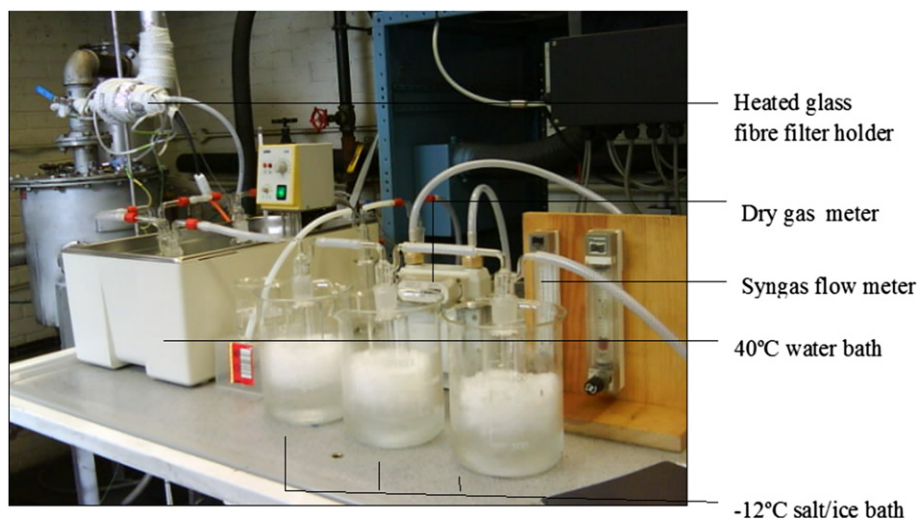
Fig. 2 — Tar collection system.

cyclone 2 were prepared as KBr pellets the pellets produced were then analysed immediately. The sample chamber of the instrument was continuously purged with high purity dry nitrogen (99.999%).

3. Results and discussion

3.1. Lignocellulosic origin of FCB tar

Fig. 3 illustrates the full infrared spectra of a typical tar sample and the associated band assignments. The spectra show the characteristic prominent C–H stretching absorption of wood at 2900 cm^{-1} and in the fingerprint region 1700—700 cm^{-1} all of the absorption bands with the exception of 1170 cm^{-1} are characteristic of the guaiacylpropane, syringylpropane and 4-hydroxyphenyl propane units which are the monomeric units of lignins and from which typical pyrolysis products such as

methylguaiacol and guaiacol are formed [17]. According to Ref. [18], the particularly strong signal at 1708 cm^{-1} is typical of C=O stretching in hardwood lignin. The absorption band at 1170 cm^{-1} is the sole band characteristic of cellulose. Band assignments for the FTIR spectrum shown in Fig. 3 are summarised in Table 2. Band assignments are in confirmation with those reported previously [18—20].

This spectrum shows that the majority of the tar produced was derived primarily from aromatic ring compounds. These compounds are based on the guaiacyl and syringyl ring monomer units of lignin and must therefore have been formed from the primary tars produced during thermal conversion of lignin. It is evident therefore that the tar produced is almost entirely lignin-derived tar.

According to Ref. [21] who investigated tar production during fixed bed gasification of wood chips the conversion of primary tars to aromatics particularly polyaromatic hydrocarbons (PAHs) becomes increasingly important at temperatures higher
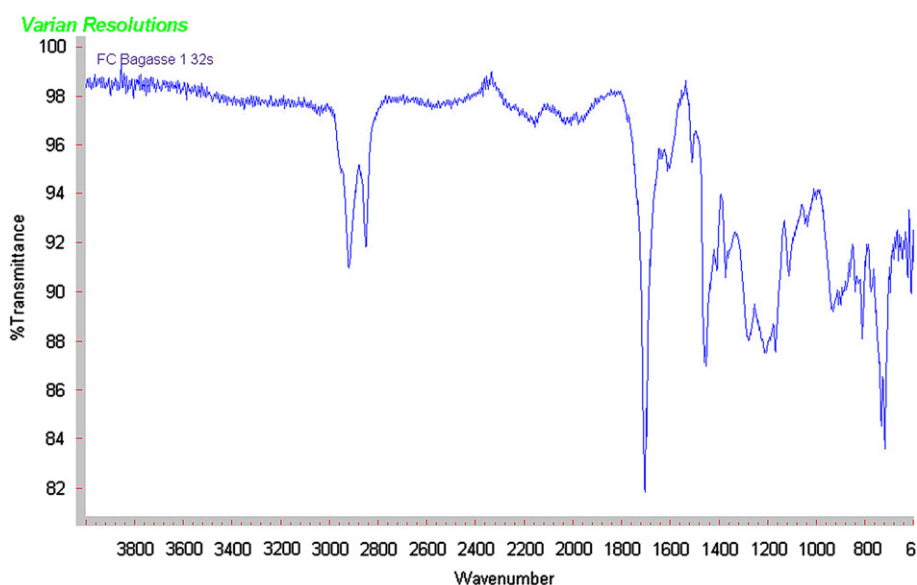

Fig. 3 — Typical FTIR spectra of tar from gasification of fuel cane bagasse.

Table 2 – Band assignments for FTIR spectrum of fuel cane bagasse tar.

Band (cm^{-1})	Band origin (assignment)
2920	C–H stretching in methyl and methylene groups in lignin [19]
2850	Symmetric CH$_2$ valence vibration in hardwood lignin [18]
1708	C=O stretch (unconjugated) seen in hardwood lignin [18]
1605	Aromatic skeletal vibration + C=O stretch of syringyl ring [19]
1514	Aromatic skeletal vibration of guaiacyl ring [19]
1463	C–H deformation; asymmetric in –CH$_3$ and –CH$_2$ [19]
1411	Aromatic skeletal vibration [19]
1377	C–H deformations (symmetric) [19]
1280	Guaiacyl ring breathing with C–O stretching [19]
1214	C–O of guaiacyl ring [18]
1170	C=O in ester group; typical of guaiacyl, syringyl and 4-hydroxyphenyl propane lignin units [20]
1116	C–O and C–C stretching and CH$_2$ rocking in cellulose [20]
938	Pyran ring vibration [19]
814–721	O–H bend and/or out of plane aromatic C–H bend [20]

Table 3 – Classification of tar compounds.

Tar class	Classification	Tar compounds
Class 1	GC-undetectable	Very heavy, 7 and higher ring compounds
Class 2	Heterocyclic aromatics	Cyclic hydrocarbons with heteroatoms, highly water soluble e.g. phenol, cresol and pyridine
Class 3	Light aromatic	Compounds that usually do not cause problems as a result of condensation or water solubility e.g. toluene, styrene and xylene
Class 4	Light polyaromatic	2 and 3 ring compounds that condense at intermediate temperatures at relatively high concentrations e.g. naphthalene, Phenanthrene and anthracene
Class 5	Heavy polyaromatic	4–6 ring compounds that condense at high temperature and low concentrations e.g. fluoranthene, pyrene, chrysene, perylene and benzo(*ghi*) perylene

than 750 °C. Since the typical operating temperature in the oxidation zone was in the range 910–1170 °C, it is likely that in this high temperature environment, secondary tar reactions which include polymerisation and condensation reactions would occur. It is these reactions which therefore result in the production of tar dominated by PAHs. Elucidation of the specific composition of the tar produced was investigated using GCMS.

3.2. Tar composition and dew point

GCMS analysis showed that the average total tar mass concentration in the raw fuel gas (identified and unidentified species) was 376 ± 27 mg m^{-3} dry gas (273.15 K, 101 kPa) which represents an average of 1.4% of the mass of the fuel.

Since the focus of this study is the production of raw fuel gas for use in power production, the tar classification system developed by Ref. [22] is used here as it is based on the performance of tar compounds in downstream processes and focuses on the condensation behaviour and water solubility of these compounds. This system which classifies tars into five classes is listed in Table 3. The percentage composition of the tar compounds collected during gasification of FCB and their tar classes are listed in Table 4.

The tar composition outlined here differs significantly from the generalised tar composition outlined by Refs. [23,24] of typical biomass gasification tars in which benzene, toluene and naphthalene accounted for mass fraction 37.9, 14.3 and 13.9% respectively and four-ring PAHs only represented a mass fraction of 0.8% of the total tar produced. This finding reinforces the need for evaluation of the typical tar composition of biomass fuels under specific gasification conditions. This will ensure that the most appropriate tar reduction processes are used to effectively reduce the quantity of tar

produced and to maximise the cold gas efficiency of the system and the low heating value (LHV) of the raw fuel gas.

Table 5 outlines the detailed tar analysis data collected during several experimental runs over 9 h of operation in which 195 kg of FCB was gasified. The number of tar species found during the runs investigated ranged from 16 to 29 tar species, all of which were identified with the exception of two compounds. The tar classes of the 2 unknowns were estimated by comparison of their total ion chromatograms with those of the identified compounds.

Table 5 clearly shows that the most common tars produced during gasification of this feedstock were Class 2 tars 4-methyl phenol and 1,2-benzediol, Class 3 tars styrene and m-xylene and Class 5 tar pyrene, together these compounds accounted for 39% of the total GC-detectable tar. The average tar dew point calculated for FCB was in the range 90 ± 5 °C. The mass fraction of pyrene was 6% of the total GC-detectable tar and since Class 5 tars dominate the tar dew point, the concentration of this along with fluoranthene and Class 4 tars

Table 4 – Overall percentage composition of tar components in fuel cane bagasse tar.

Compound	Composition, $w_{\text{composition}}$ (% db)			
1-Ring aromatic hydrocarbons	36.9			
2-Ring aromatic hydrocarbons	6.2			
Heterocyclic compounds	2.4			
Phenolic compounds	29.2			
3-Ring PAHs	18.8			
4-Ring PAHs	6.6			
Tar class	2	3	4	5
Composition, $w_{\text{composition}}$ (% db)	32 ± 16	35 ± 6	18 ± 9	12 ± 9

Tar class	Tar component	GC-detectable tar (mg m^{-3})[a]					
		1	2	3	4	5	6
2	3-Phenoxy-1,2-propanediol	90.4	32.6	*	*	11.9	6.1
	4-Methyl phenol	117.8	48.1	35.4	28	*	11.8
	Dimethyl phenol	46.2	30.6	*	*	*	6.5
	1,2-Benzenediol	388.8	22.7	35.5	25.3	*	36.4
	3-Nitropyridine	148.8	*	*	*	*	14.2
	3-Hydroxybenzylalcohol	252.1	20.5	*	*	*	22
	2,6-Dimethoxy phenol	185.6	20.7	27.5	*	*	24.4
	Dibenzofuran	110.4	*	*	*	*	12.4
	2-Methoxy-4-(1-propenyl) phenol	101.4	*	*	*	*	12.6
	Unknown	72.1	*	27.7	*	*	11.480
	3,5-Dimethoxy-2,4-dimethyl phenol	57.2	*	29.4	*	*	6.8
	Unknown	38	*	*	*	*	8.4
	2-Hydroxy-4,6-dimethoxy acetophenone	50.8	*	29.8	*	*	7.9
3	m-Xylene	17.661	49.8	37.7	30.3	12.3	*
	Styrene	*	86.4	50.7	31.4	17.5	2.9
	α-Methyl benzene methanol	275.4	25.6	*	*	*	24.4
	2,4,6-Trimethyl benzeneamine	44.7	19.5	*	*	11.4	22.3
	2,3,4-Trimethoxybenzaldehyde	*	19.6	28.5	*	*	13.8
	3-Hydroxybenzaldehyde	99.4	20.7	27.0	*	*	10.6
	1,4-Dimethoxybenzene	157.17	*	*	24.9	*	16.1
	3-Hydroxy-4-methoxybenzaldehyde	82.8	*	*	*	*	8.8
	2-Methoxy-5-methyl-benzenamine	61.7	*	27.7	*	*	6.6
	3-Formyl-2-methyl indole	*	*	27.4	*	*	3.9
4	Acenaphthalene	*	10.8	*	12.1	6.4	1.5
	Fluorene	55.4	15.6	23.8	19.8	9.6	5.2
	Benz[a]anthracene	26.4	*	*	*	*	3.7
	Phenanthrene	105.5	19.9	29.8	23.7	11.4	3.2
	Anthracene	36.5	*	36.2	30.1	*	3.3
	4,5-Methylenephenanthrene	38.6	*	*	*	*	*
	9,10-Bis(chloromethyl) anthracene	37.2	24.5	*	*	*	*
5	Fluoranthene	*	17.8	28.8	19.6	10.7	2.3
	Pyrene	72.5	26	36.7	31.9	16.5	3.5
Tar dew point (°C)		117.2	87.2	96.2	93.7	81.8	92.7

Table 5 − GC-detectable tar in syngas from gasification of fuel cane bagasse.

a 273 K, 101 kPa.

fluorene and phenanthrene represent the primary contributors to the high tar dew points observed.

The tar dew point is an important thermodynamic property which indicates the potential for condensation of a given composition of tars. It is defined as the temperature at which the real total partial pressure of tar equals the saturation pressure of tar [22]. When the actual temperature of the downstream raw fuel gas users falls below the thermodynamic dew point, tar can condense out of the raw fuel gas. The tar dew point values presented here were calculated using the tar dew point model developed and validated by the Energy Research Centre of the Netherlands (ECN). This model has an accuracy of ±3 °C in the temperature range 20−170 °C and is the sum of all the dew point values of compounds with molecular weights between toluene and coronene [25].

$$22,400 \frac{C}{M} \frac{T}{273} \frac{1}{p_{sv}(T)} = 1 \qquad (1)$$

where C = concentration of compound in g m^{-3}; M = molecular weight of compound; $p_{sv}(T)$ = saturated vapour pressure of compound at temperature T.

The relationship between the tar dew point and the tar classes as categorised by Ref. [22] is illustrated in Fig. 4. which shows that even at concentrations of approximately 0.1 mg m^{-3} (273.15 K, 101 kPa) Class 5 tars have a tar dew point of 120 °C. This exceeds the dew point at which concentrations in excess of 1000 mg m^{-3} (273.15 K, 101 kPa) of Class 2, 3 and 4 would condense. It can also be seen that even at concentrations as high as 10,000 mg m^{-3} (273.15 K, 101 kPa) condensation of Class 3 tars does not occur. Determination of the tar dew point is therefore indispensable in establishing the operating conditions under which tar condensation and deposition will begin to occur upon cooling of the raw fuel gas. Furthermore it facilitates an evaluation of the potential impact on downstream equipment. Given the high incidence of occurrence of pyrene and fluoranthene this means that even at very low concentrations of these compounds in the raw fuel gas from this feedstock, condensation and deposition of the tar can occur at temperatures above 100 °C. Therefore it is necessary that in a commercial scale system formation of these tars during gasification of this feedstock is prevented or that design parameters are developed for the
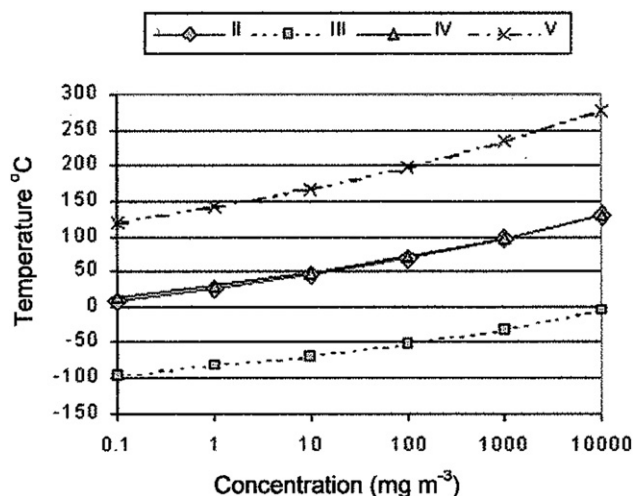
Fig. 4 – Relationship between the tar dew point and concentration of different tar classes. Source: van Paasen and Kiel [22].

Table 6 – Class 1 tar fraction in syngas from fuel cane bagasse.

Tar classification	Tar (mg m^{-3}, db)[a]				
	1	2	3	4	5
Gravimetric tar	397.33	394.68	396.08	349.38	342.53
Class 1 tar	36.25	30.51	18.96	41.22	29.73
a 273 K, 101 kPa.					

removal of these compounds from the raw fuel gas using gas cleaning systems.

3.3. Class 1 tars and gravimetric tar

The tar dew point is also influenced by Class 1 tars which are known as GC-undetectable tars since they cannot be assessed by GC methods. This class includes PAHs with more than 7 rings which are believed to start condensing at temperatures around 300–350 °C even at very low concentration [22,26]. An estimation of the Class 1 tar component is made by calculating the difference between the gravimetric tar component and the GC-detectable tar.

Gravimetric tar is defined as the evaporation residue at given and standard conditions (temperature, pressure and duration) [25] and includes both GC-detectable as well as Class 1 tars. In the present work, the gravimetric tar content was determined as outlined in Section 2.5.1. Determination of the true Class 1 tar fraction in these tar extracts was investigated by re-dissolving the gravimetric tar obtained from evaporation, analysing it for Class 2–5 tars by GCMS and calculating the difference between the total GC-detectable tar and the gravimetric tar.

The average gravimetric tar concentration in the raw fuel gas was 376 ± 27 mg m^{-3} (273.15 K, 101 kPa), of which the Class 1 tar concentration was 31 ± 8 mg m^{-3} (273.15 K, 101 kPa) which represents a mass fraction of 8% of the total tar produced. The presence of Class 1 tars in the tar produced therefore indicates that the tar dew points calculated in Table 5 underestimate the actual tar dew point in the experimental runs investigated. These high molecular weight compounds can be identified using HPLC techniques however access to this analytical technique was not available and therefore identification was not possible (Table 6).

Class 1 tars are also the primary components of soot and according to several authors including [1,27,28] compounds such as fluoranthene and pyrene which are formed to some extent by polymerisation and condensation can be considered as soot precursors. Therefore the relative percentage composition of Class 1 tars to Class 4 and 5 compounds can be used to indicate the likelihood of gravimetric tar production during gasification of biomass fuels. Both pyrene and fluoranthene have been identified in these tar extracts at 1.5 times the concentration of the Class 1 heavy organics. The percentage concentration of heavy organics relative to the Class 4 and 5 tars in the gravimetric tar indicates that the reactions outlined by Ref. [27] in which intermediates such as fluoranthene and pyrene undergo further condensation and polymerisation at increasing temperature to form Class 1 tars did not occur extensively. It must also be noted that benzene and naphthalene which have both been identified as soot precursors in Jess' reaction scheme were not found in the tar produced from this feedstock. These observations suggest therefore that high production of Class 1 tars during gasification of this feedstock under the conditions investigated is unlikely.

4. Conclusions

Similar to the presence of alkali, alkali earth metals and major ash forming elements [29], the presence of tars in syngas will affect the performance of SOFCs. The results of this investigation show that the mass fraction of tar produced during air-blown downdraft gasification of fuel cane bagasse is 1.4% of the fuel fed to the gasifier and that the typical concentration produced is within the limit for SOFCs. This finding highlights the efficiency of the secondary pyrolysis reactions occurring in the oxidation zone of this downdraft gasifier which appears to yield similar results in scaled-up versions of 1 MWe outputs [30,31].

However, although tar production is low the chemical composition is dominated by Class 2 and 5 tars; furthermore 7 ring and larger PAHs comprise a mass fraction of 8% of the tar formed which therefore imposes a high tar dew point above 100 °C even at concentrations as low as 0.1 mg m^{-3} (273.15 K, 101 kPa). On the basis of the tar composition elucidated, it can be expected that a high potential for excessive fouling of SOFC anodes could occur, this study therefore emphasises the need to assess the specific tar composition produced by biomass gasification systems so as to facilitate the design of effective and efficient raw fuel gas cleaning systems targeting the typical tar compounds produced by a given biomass. Additionally the growth of PAH compounds at high gasification temperatures is widely known and therefore the incidence of occurrence of Class 5 tars, fluoranthene and pyrene highlights the need for strict control of the equivalence ratio and the

oxidation zone temperatures during gasification of this feedstock on an industrial scale [30,31] so as to minimise the formation of these compounds.

Acknowledgements

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